



Gaseous reference standards of formaldehyde from trioxane

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ABSTRACT

We have developed a dynamic reference standard of gaseous formaldehyde based on diffusion of the sublimate of trioxane and thermal conversion to formaldehyde in the gas phase. We have also produced a gravimetric standard for formaldehyde in a nitrogen matrix, also by thermal conversion of the sublimate of trioxane. Analysis of the gravimetric standard with respect to the dynamic standard has confirmed the comparability of the static and dynamic gravimetric values.

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1. Introduction

In view of its widespread use, toxicity and volatility, measuring exposure to formaldehyde is a significant consideration for the protection of human health. [1] It also plays an important role in the chemistry of the atmosphere as it is a significant source of HO_x radicals, the key oxidant in the troposphere. [2] For this reason, formaldehyde is one of the target compounds for the Global Atmospheric Watch (GAW) programme of the World Meteorological Organisation (WMO) which provides reliable scientific data and information on the chemical composition of the atmosphere [3]. Reference standards of formaldehyde are therefore required for studies of toxicological effects, and to underpin the development and testing of analytical methods for the environmental monitoring of important atmospheric processes.

Several methods have been reported for generating gaseous mixtures of formaldehyde. These include the gas-phase reaction of ethene and ozone [4] and the catalytic conversion of methanol [5]. An alternative approach involves the depolymerisation of a formaldehyde polymer such as para-formaldehyde [4] or a mixture of polymers such as alpha-polyoxymethylene (POM) [6–9]. The difficulty presented by these methods is the generation of a gas flow that is solely in the monomeric form and is free from the release of any bound water. For example, the sublimation of POM typically gives rise to as much as 10% trioxane (a cyclic trimer of formaldehyde) and water, the latter is chemically bonded into the POM at the level of approximately 4%. Recent

work at National Metrology Institutes (NMIs) has focussed on the use of a permeation tube of POM for the generation of reference standards of formaldehyde in nitrogen. This has the advantage that the amount of formaldehyde can be determined from the loss of mass from the permeation tube, but the disadvantage that some part of the lost mass is due to polymers and water as described above. Another method which was developed to produce percentage-level concentrations of formaldehyde in air is the vapour phase depolymerisation of trioxane. [10] The method involved bubbling air through molten trioxane and passing the vapour through a catalyst. Conversion yields to formaldehyde as high as 89% were reported. Higher yields were expected, but not obtained, due to some re-polymerisation of the formaldehyde [11]. Since its initial development, this method has been modified and a conversion efficiency close to 100% has been reported [12,13]. This approach has the benefit that high purity trioxane is readily available for use as the source material. Its formula is better defined than other mixtures of polymers of formaldehyde such as POM and the amount fraction of water chemically bonded into the solid is considerably less.

A variety of methods have been used to measure formaldehyde. Perhaps the most widely used for ambient air monitoring and atmospheric research is sampling with adsorbent cartridges of 2, 4-dinitrophenylhydrazine, followed by HPLC separation and UV detection. Other methods include spectroscopic methods such as cavity ring down spectroscopy (CRDS), and gas chromatography (GC) using helium ionisation detection (HID) [14], pulsed discharge ionisation detection (PDID) [15] or a pulsed helium ionisation detection (pHID) [16]. More recently, a microfluidic lab-on a chip technique has been developed to achieve a rapid and sensitive determination of the ambient gaseous formaldehyde when used in combination with GC-MS.[17] However all require calibration and traceability to reference standards.

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In this paper we report a novel method for the preparation of static reference standards of formaldehyde from diffusion of the sublimate of trioxane followed by thermal conversion. We also report on the validation of these standards against a dynamic reference standard of formaldehyde generated by the same diffusion and thermal decomposition processes. In the following section we describe both methods and show how the uncertainty of the generated amount fractions of formaldehyde can be estimated. We then report a comparison of the static reference standards to the dynamic standards using a CRDS analyser.

2. Materials and methods

2.1. Generation of formaldehyde

The sublimate was thermally dissociated to formaldehyde by passing it through 1.5 m of temperature-controlled 1/16 in. silico steel. A residual gas analyser (Kurt J Lesker, AccuQUAD) was used to monitor the purity of the formaldehyde leaving the heated tubing. Hence, the efficiency of conversion of trioxane vapour to formaldehyde could be determined.

Experiments with the thermal converter indicated that 230 °C was the optimum temperature for conversion. Any increase in temperature above this produced some breakdown of the formaldehyde to CO and CH₄, whereas lower temperatures resulted in reduced conversion of the trioxane to formaldehyde. The purity of the gas generated at 230 °C from the thermal conversion of the trioxane was determined by diluting the formaldehyde in helium followed by analysis by GC–MS (Agilent) using a 75 m column with a 0.53 mm diameter (DB 624, Agilent). The purity was shown to be 99.5% with the impurities including CO₂, N₂ and some residual dimer (methyl formate) but no measurable trioxane. The chromatogram is shown in Fig. 1.

2.2. Preparation of static standards

Several static reference standards were prepared from the flow of formaldehyde generated with the trioxane conversion process described above. A schematic of the equipment used for their preparation is shown in Fig. 2. A granule of phosphorous pentoxide (P₄O₁₀, Sigma Aldrich Company Ltd) was placed into a transfer loop (a piece of 1/8 in. diameter tubing with Swagelok fittings on each end). A pellet of 1,3,5 trioxane (Acros Organics 99.5+%, 4–5 mm in length) was formed and added to the transfer loop. The transfer

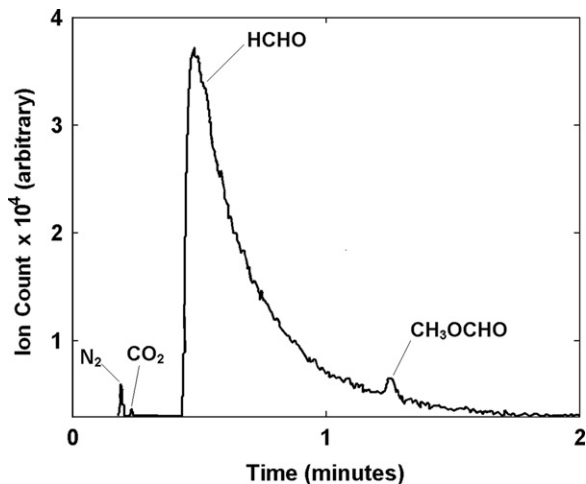


Fig. 1. GC–MS analysis of trioxane in helium after passing over a converter at 230 °C. The total ion count across the mass range vs retention time is shown.

loop and a vacuum pump were connected to a two way valve (positions B and C in Fig. 2(a) respectively). Valve 2 was adjusted to position 2 and valve 1 was then opened to evacuate the transfer loop and remove any air present on the surface of the trioxane. When a pressure of 4×10^{-3} mbar was achieved, valve 1 was closed and valve 2 was adjusted to position 1. The transfer loop and valve 2 were disconnected from the vacuum line and weighed. A converter (as described previously) was then connected to position C on valve 2 as shown in Fig. 2(b). The converter was set to the optimum conversion temperature of 230 °C (determined previously). The output of the converter was connected to a minimised dead volume (mdv) valve on an evacuated cylinder ((10L, BOC spectraseal). The vacuum line was connected to position A and valve 1 was opened to evacuate the line between valve 2 and the cylinder (valve 2 was still in position 1). Valve 1 was then closed and valve 2 was set to position 2 to open the line between the transfer loop and the evacuated cylinder. The cylinder valve was then opened to enable the transfer of trioxane via the converter to the cylinder. In order to prepare a mixture containing 10 μmol/mol HCHO in a matrix of N₂, the system was left for approximately 8 h in order to transfer 13.4 mg of trioxane. This was calculated from the vapour pressure of trioxane at 20 °C [18]. When the transfer was complete, valve 2 was adjusted to a half way position between 1 and 2. A wait time of two minutes was employed to allow the transfer of trioxane/formaldehyde from the capillary to the cylinder. After this time the cylinder valve was closed. The transfer loop and valve 2 were then weighed after being disconnected from the converter and the cylinder. The cylinder was then weighed. To prevent re-polymerisation of HCHO, the cylinder was filled in two stages. Initially with 10 bar of N₂ and then with 90 bar of N₂. After each addition of N₂ the cylinder was rolled for 20 min. After the second filling of N₂ the cylinder was re-weighed.

2.3. Dynamic reference standards

A schematic diagram of the diffusion system used to generate formaldehyde from trioxane is shown in Fig. 3. Approximately 5 g of trioxane was pressed into small rods and placed in a borosilicate glass cell. Diffusion was governed by a glass capillary 79 mm long and with 4.9 mm inside diameter. The cell was designed to generate trioxane at a rate of approximately 700 μg/h [12]. The cell was placed in an oven at 35 °C together with a thermal converter operated at 230 °C (as described previously) and a heat exchanger. The heat exchanger was 2.5 m of 1/16 in. silico steel tubing and served to equilibrate the incoming nitrogen to the temperature of the oven before reaching the diffusion cell. A flow of approximately 0.75 l/min of nitrogen (BOC, oxygen free) was passed into the system using a mass flow controller (MKS, 5 l/min full scale) and was measured using a high accuracy Dry-Cal Flow Calibrator (ML-800, Bios International Corporation) under controlled conditions. Prior to entering the oven, the flow was split into two paths (shown with solid grey and black lines in Fig. 3). The solid grey pathway flows at approximately 0.02 l/min through the heat exchanger and then through the diffusion cell. Trioxane in the vapour phase is removed from the cell by the balance gas flow and is converted to formaldehyde by the thermal converter. The solid black pathway flows at approximately 0.7 l/min and dilutes the output from the converter. A mixture of approximately 10 μmol/mol formaldehyde in the matrix of nitrogen is generated and analysed by CRDS (Picarro G1107).

The mass loss of trioxane from the diffusion cell was measured periodically over an 8 month period and is shown in Fig. 4(a) (left axis). The data have been fitted with a quadratic polynomial and the residual deviations are shown with crosses (right axis). The dispersion of the residuals is within the range ± 2 mg. The diffusion rate at any point in the 8 month period has been

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